SECTION C
Organic Chemistry

The Reaction of Grignard Reagents with *N*-Substituted Maleimides

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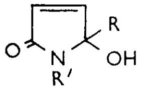
Arylmagnesium bromides react with *N*-substituted maleimides to yield *N*-substituted-5-aryl-5-hydroxy-2-pyrrolinones and not the corresponding open chain β-aroylacrylamides. The structural assignments are based on ultraviolet, infrared, and nuclear magnetic resonance spectra.

AWAD and co-workers[1] have recently reported that the reaction of molar equivalents of Grignard reagents and *N*-arylmaleimides leads to β-aroyl-*N*-arylacrylamides (I; R = R′ = aryl). We now wish to present evidence that the products of such reactions are, on the contrary, the corresponding hydroxypyrrolinones (II).

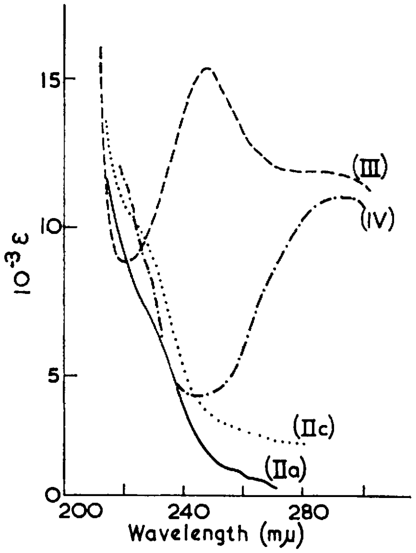
RCO–CH=CH–CO–NHR′
(I)


(II)

(a, R = Ph, R′ = Me; b, R = Ph, R′ = Et; c, R = R′ = Ph; d, R = *p*-MeC_6H_4, R′ = Ph; e, R = *p*-MeC_6H_4, R′ = Et)

N-Substituted maleimides have been treated at room temperature with molar equivalents of ethereal arylmagnesium bromides to give colourless products whose formulæ are consistent with either of the two sets of structures (I) or (II). Analytical data and melting points are given in Table 1. All of these compounds, including Awad's compounds (I) or (II); (c) and (d), readily yielded 2,4-dinitrophenylhydrazones. This does not necessarily confirm the keto-amide structures (I) since ready ring opening of the cyclic molecules (II) could lead to the same results. Indeed, the ultraviolet spectra of the compounds are not at all similar to the spectrum of β-benzoylacrylic acid, which is reported[2] to have a broad, intense band at 238 mμ. Moreover, the free benzoyl group in a variety of different compounds has been shown to absorb strongly near 240 mμ[3-5] and the absence of such absorption for *cis*-3-benzoylcinnamic acid[4] and 3-benzoyl-2-cyanocinnamamide[5] has been considered compelling evidence for the existence of these and similar compounds as hydroxylactones and hydroxylactams, respectively. Hence, the spectra of the present compounds cast doubt on their formulation as open chain structures.

The infrared spectra of two of the compounds (IIb and c) were measured in Nujol mull using a Perkin-Elmer model 21 spectrophotometer. The results are given in Table 2. Both substances gave rise to a single strong carbonyl band near 5·92 μ, a result favouring the cyclic formulation. The carbon–carbon double bond absorption appeared on this peak as a shoulder near 6·0 μ. A rather broad, weaker band near 3·1 μ is attributed to OH stretching vibrations rather than NH absorption, as Awad assumed. Similar spectra have been previously observed for related 3-substituted-5-hydroxy-2-pyrrolinones.[5,6]



Ultraviolet spectra in ethanol of compounds (IIa; R = Ph, R′ = Me), (IIc; R = R′ = Ph), (III) ethyl 3-benzoyl-2-cyanocinnamate, and (IV) 4-cyano-2,3-diphenyl-2-hydroxy-5-oxo-Δ^3-pyrroline

The nuclear magnetic resonance (n.m.r.) spectra of the same two compounds have been measured in acetone solution using a Varian model DP-60 spectrometer incorporating an internal lock to TMS. In both cases, the resonance of the ethylenic hydrogens was an AB quartet with J_{H-H} approximately 6 c./sec. Therefore, the structures must be cyclic since otherwise this value

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TABLE 1

N-Substituted-5-aryl-5-hydroxy-2-pyrrolinones

Compound	Yield (%)	M. p.	Found (%) C	Found (%) H	Found (%) N	Formula	Requires (%) C	Requires (%) H	Requires (%) N	ε at 240 mμ
(IIa) [a]	76	158°	69·9	5·7	7·3	$C_{11}H_{11}NO_2$	69·8	5·8	7·4	3922
DNP [b, c]		261	55·3	4·3	18·8	$C_{17}H_{15}N_5O_5$	55·3	4·1	19·0	
(IIb) [d]	83	134	70·7	6·2	6·9	$C_{12}H_{13}NO_2$	70·9	6·4	6·9	3645
DNP [b, c]		215—220, decomp.	56·4	4·4	18·3	$C_{18}H_{17}N_5O_5$	56·0	4·1	18·8	
(IIc) [d, e]	78	143	76·3	5·1	5·5	$C_{16}H_{13}NO_2$	76·5	5·2	5·6	5221
DNP [b, c]		225, decomp.			16·0	$C_{22}H_{17}N_5O_5$			16·2	
(IId) [e]	72	168				$C_{17}H_{15}NO_2$				5386
(IIe) [f]	40	120	71·7	6·8	6·3	$C_{13}H_{15}NO_2$	71·9	6·9	6·4	4981
DNP [b, c]		212			17·9	$C_{19}H_{19}N_5O_5$			17·6	

[a] From benzene. [b] From isopropyl alcohol/acetic acid (4 : 1). [c] 2,4-Dinitrophenylhydrazone. [d] From benzene–light petroleum (60—80°) (2 : 1). [e] See reference 1. [f] From carbon tetrachloride.

would be between 10 and 12 c./sec.[7] The present values may be compared with those for cyclopentene (J_{H-H} = 5·3 c./sec.) [8] and maleic anhydride (J_{H-H} = 5·7 c./sec.).[9]

TABLE 2

Spectra of *N*-substituted-5-aryl-5-hydroxy-2-pyrrolinones

Compound	Infrared absorption (μ) OH [a]	Infrared absorption (μ) C=O [b]	Infrared absorption (μ) C=C [c]	N.m.r. absorption C=C τ_1	N.m.r. absorption C=C τ_2	N.m.r. absorption C=C J_{H-H} c./sec.	N.m.r. absorption OH τ
(IIb)	3·17	5·94	6·00	3·1	3·9	6·0	4·3
(IIc)	3·04	5·92	5·98	2·9	3·8	6·1	3·7
(II; R = R′ = H) [d]				3·1	3·9		5·2

[a] Broad band. [b] Strong peak. [c] Shoulder. [d] In $CDCl_3$, see ref. 10.

Both compounds gave rise to a sharp peak near 4 τ, indicating the presence of an OH rather than an NH group, for which a broad band would be expected. 5-Hydroxy-2-pyrrolinone (II; R = R′ = H) has given similar results.[10]

Awad and co-workers appear to have overlooked previous evidence [11,12] that Grignard reagents and *N*-substitued succinimides undergo reaction to form hydroxypyrrolidones, and other indications [5,11,13] that γ-keto-amides usually exist in cyclic forms.

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